

Accelerated Aging Tests on Alum-Retanned Vegetable Leathers*

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Previous studies^{1,2} have shown that vegetable leathers retanned with alum have a high resistance to acid deterioration and that this and other properties of such leathers make them potentially useful for many purposes. This study presents further data on the acid resistance of various types of alum-retanned leather.

The leathers used in these tests may be considered in three groups: First, some laboratory tanned leathers on which we have previously reported physical and chemical data²; second, commercially tanned rough belting leather retanned in the laboratory with alum and with chrome; and third, sheepskin leathers tanned with quebracho and retanned with alum by a

*Presented at the Thirty-Ninth Annual Meeting, Columbus, Ohio, June 2, 1942.

commercial tanner. The first group consisted of those leathers referred to as "steer hide II," "calfskin II," and "sheepskin" in our previous paper². Each set consisted of a vegetable control leather, a vegetable leather retanned with alum, and one retanned with chrome. The method of tannage and the physical and chemical data have been discussed in our previous paper².

For the preparation of the second group of leathers, a piece of commercially tanned rough belting leather was divided into four pieces, each about 8 by 12 inches. One piece was used without further treatment as a control. The remaining pieces were thoroughly washed with water. One of them was used for a further control, called "washed vegetable leather" to distinguish it from the first sample, which was identified as the "unwashed vegetable leather." One of the remaining pieces was alum retanned and the other chrome retanned. For the alum retannage the same type of liquor was used as in previous tests, namely, a solution of aluminum sulfate one-fourth neutralized with sodium carbonate and containing sodium chloride equal to the amount of aluminum sulfate. For the chrome retannage a chrome-alum solution one-third neutralized with sodium carbonate was used. The leathers were neutralized by remaining in a dilute sodium bicarbonate solution until equilibrium was reached at about pH 4.5; they were then washed with water, oiled with neats-foot oil, and dried.

The third group of leathers consisted of three sheepskins in which the complete operations of tanning with quebracho, retanning with alum, and fat-liquoring were performed by a commercial tanner.

Some of the analytical figures for the first group have already been given². Similar figures for the second and third groups are given in Table I.

TABLE I
ANALYSES OF LEATHERS (*Moisture-Free Basis*)

Description of Leathers	Total Ash	Al ₂ O ₃ or Cr ₂ O ₃	Soluble Non-tannin	Soluble Tannin	pH	Degree of Tannage
Group II:	Per Cent	Per Cent	Per Cent	Per Cent		
Unsplit, unwashed, vegetable.....	0.3	..	2.7	5.8	3.60	78
Unsplit, washed, vegetable.....	0.2	..	1.5	4.9	3.70	77
Unsplit, alum-retan.....	4.3	2.7	4.8	1.9	3.78	84
Unsplit, chrome-retan.....	3.9	3.6	1.3	1.2	3.68	82
Grain split, vegetable.....	0.2	..	1.8	4.8	3.71	88
Grain split, alum-retan.....	4.2	3.3	3.4	1.5	3.82	90
Grain split, chrome-retan.....	5.2	4.0	1.7	1.6	3.68	86
Middle split, vegetable.....	0.1	..	1.7	5.0	3.65	69
Middle split, alum-retan.....	3.3	1.9	4.2	2.0	3.66	72
Middle split, chrome-retan.....	3.6	3.4	0.8	0.7	3.61	78
Flesh split, vegetable.....	0.4	..	1.6	4.8	3.81	71
Flesh split, alum-retan.....	5.1	3.7	5.8	2.3	3.82	90
Flesh split, chrome-retan.....	4.2	3.1	2.5	2.3	3.63	77
Group III:						
Skin I, alum-retan.....	4.5	3.6	2.6	2.2	4.05	56
Skin II, alum-retan.....	3.2	3.1	1.0	0.9	4.07	56
Skin III, alum-retan.....	3.0	3.0	1.3	1.2	4.05	54

The leathers were exposed for accelerated aging in the gas chamber, previously described³. According to our usual practice, alternate strips were exposed and the remaining strips were used as controls. Since the retanned belting leather was considerably thicker than the samples ordinarily used in our tests, the samples after tannage and before exposure were split into grain, middle, and flesh layers of approximately equal thickness. Some of the unsplit leather was also exposed. The exposure period was fifteen weeks for groups I and II and eighteen weeks for group III. The unexposed and exposed leathers were then tested for tensile strength, pH values by the glass electrode, and sulfur by the bomb method. Soluble nitrogen was determined by extraction first with water at 50° C. and then with 0.1 *N* sodium carbonate at room temperature. The loss in tensile strength of the exposed pieces as compared with the corresponding unexposed controls is expressed as percentage deterioration. The data on these tests are given in Table II.

The results of these tests confirm our previous findings. The alum-retanned leathers have a considerably higher resistance to acid deterioration than the chrome-retanned leathers, which in turn are markedly superior to the straight vegetable leathers. The data on soluble nitrogen are in agreement with those on physical deterioration. The pH values of the exposed alum leathers are particularly to be noted. They are all high—considerably higher than either the vegetable or chrome leathers—and this difference cannot be accounted for by the difference in acid pick-up. The alum retannage apparently exerts a buffering action, preventing a rapid drop in pH with absorption of acid.

One point in the data on the split belting leather may indicate a significant difference in the tanning action of chrome and alum liquors. The middle layer of the vegetable or chrome leathers is more resistant than either the grain or flesh layer. The reverse is true for the alum leather. The explanation is that the amount of Al_2O_3 in the middle layer is low, as compared with the other layers, whereas in the chrome leather the difference in Cr_2O_3 content between the three layers is small. This is an indication that the alum liquor penetrates the leather more slowly than chrome liquor does. This fact may prove to be of importance in tannery practice.

The first group of leathers were completely tanned in the laboratory. In the second group the work has been extended into actual tannery practice by using leather which had been commercially vegetable tanned. In the third group the complete tannage has been carried on in the tannery by usual tannery practices. The results show that alum retannage can be accomplished as successfully in practice as in the laboratory.

Conclusions

Previous findings on the high resistance of alum-retanned vegetable leathers to acid deterioration have been confirmed.

The practicability of actual tannery production of this type of leather has been demonstrated.

REFERENCES

1. The Permanence to Acid Deterioration of Vegetable Leather Retanned with Alum. *J.A.L.C.A.*, 35, 440 (1940).
2. Physical Properties of Alum-Retanned Vegetable Leather. *J.A.L.C.A.*, 37, 478 (1942).
3. A Proposed Standard Gas Chamber for Accelerated Aging of Leather. *J.A.L.C.A.*, 35, 180 (1940).

Discussion

E. L. WALLACE: In discussing this paper I would like to bring up this question: how will "straight" alum-tanned leather age?

J. S. ROGERS: I don't have the figures now; but, if I remember correctly, the alum-tanned leathers do stand up.

WALLACE: We have a paper following this one which confirms some of these results.

There is one thing we have noticed: the alum retan has a buffering action against acid. What this leather will do in an oxidizing atmosphere I don't know. Dr. Kanagy has developed an accelerated aging test different from that used by Dr. Frey, in which he used moisture, oxygen, and heat. We have obtained some unexpected results with this method. For example some leathers which will stand the shrinkage test and the boiling test, will show a large deterioration under these accelerated aging conditions.

R. M. KOPPENHOEFER: How was soluble nitrogen determined?

ROGERS: Alkaline solution and water. The first is a 50° C. water solution and then an 0.1 N sodium carbonate solution.

KOPPENHOEFER: Secondly, I would like to ask if vegetable controls you ran were oiled the same as the alum ones?

ROGERS: Yes.

V. J. MLEJNEK: I would like to ask Dr. Rogers if, in the soluble nitrogen determination, the determination is made on various sections of the same skin or hide, are the results comparable? For instance, the backbone section as compared with the flank or the belly section of the same hide?

ROGERS: We have not made a study of the different sections of the different hides in that way. That is something that would have to be taken up later on. The samples were taken from the skin in such a way as to be comparable.

WALLACE: I might answer that. We have checked this point in our work, and have found very little variation over the entire hide.

A. SCHUBERT: In your tables you show degree of tannage figure. How did you calculate that? The laboratory tannage showed one with 50 per cent higher than the practical tannage.

ROGERS: It was done by the A.L.C.A. method.

A. H. WINHEIM: Dr. Koppenhoefer's question might have been along the same line; but, if not, I would like to ask this: Did you say that the original

laboratory-tanned leathers reported in your first paper were not fat-liquored, and that in this particular series they were fat-liquored for subjecting to aging tests?

ROGERS: The laboratory leathers were not fat-liquored, but they had an oil treatment.

The leathers were neutralized by remaining in a sodium carbonate solution until equilibrium was reached, then washed with water, oiled with oil, and dried.

R. L. MOORE: A number of years ago a company that I was associated with put out compounds for use in conditioning sole leather. In the early '20's, one of them contained a large amount of aluminum sulfate. The leather that was produced by its use was extremely durable and had a very low rate of absorption of water, so it could be worn for a long time under wet conditions and the shoe would not lose its shape. The product was discontinued after a year or so, because it gave a greenish-yellow color tone to the leather. The leather produced by its use was one of the best for durability and water-resistance that I have ever seen.

H. B. WALKER: I might add briefly that I think the instigation of the queries about the oiling of these leathers may have sprung from the idea that the oiling would have an influence on the degree of acid deterioration. In the work done on acid deterioration some years ago at the Bureau of Standards, if I recall correctly, Mr. Wallace, the proof was rather conclusive that oiling had no effect at all on the amount of deterioration.